

## PATENT SPECIFICATION

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## (54) REINFORCED PLASTICS MATERIALS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the production of reinforced composites from thermosettable resins in film form and certain reinforcing materials. It is an improvement in, or modification of, the invention described and claimed in our British Patent No. 1,299,177.

In British Patent No. 1,299,177 there is claimed a method of making a reinforced composite which comprises bringing together an essentially solid continuous film comprising a thermosettable resin composition and strands of unidirectional reinforcing material in the form of fibres of at least one of glass, boron, and carbon under conditions such that the resin composition flows about the strands, and the resin composition and the strands form a coherent structure.

Reinforced composites made in this way are generally satisfactory but not always entirely so. In particular, they need to be handled with care if they are to retain their structural integrity. Further, when they are formed into a curved shape they show a tendency to separate along the direction of the fibres. Such separation severely weakens any structure made from the composites. It follows that any curved structure made from a unidirectional fibre-reinforced composite must receive special treatment in the area of the curves during manufacture, to prevent this separation from taking place.

There is therefore a need for a unidirectional composite which retains all the advantages of the aforesaid composites but which may be handled without the need for special precautions to prevent separation along the direction of the fibres.

We have now found that this object may be achieved if, in the manufacturing process, a layer of fibrous material having structural integrity and the unidirectional fibres are brought together and both are then impregnated with a solid film adhesive to form a coherent structure. This process may be used not only with unidirectional glass, boron, or carbon fibres but also with other unidirectional fibres such as polyamide, especially aromatic polyamide, fibres, and metal filaments, e.g., of tungsten.

Accordingly, one aspect of this invention provides a method of making a reinforced composite which comprises bringing together an essentially solid continuous film comprising a thermosettable resin composition, strands of unidirectional reinforcing material, and a layer of fibrous material having structural integrity, under conditions such that the resin composition flows about the strands and fibrous material and forms a coherent curable structure.

The above-mentioned British patent discloses the formation of multilayer composites having layers of reinforcement additional to the unidirectional strands. Impermeable materials, viz., plastics and rubber films and metal foils, are the only materials mentioned as examples of such additional reinforcement. In the process of the present invention, on the other hand, the continuous layer of fibrous material having structural integrity is permeable, allowing the resin film to pass around the fibres and impregnate this layer, forming a coherent structure.

Another aspect comprises reinforced composites made by the method of this invention.

The resin composition is caused to flow about the strands and the fibrous material by the application of heat and/or pressure. Generally, temperatures of 50° to 180°C and pressures of 150 to 1000 kPa are employed; temperatures of 100 to 140°C

and pressures of 300 to 600 kPa are particularly preferred. It is essential that the heating is insufficient to convert the resin into the fully cured, insoluble, and infusible C-stage, but rather that the resin remains in the A-stage or is, at most, advanced only to the B-stage. The terms "A-, B-, and C-stages" used herein are as defined in ASTM D 883-73a. The resin may be subsequently converted into the fully cured, insoluble, and infusible C-stage when required, e.g., after the composite has been formed into some desired configuration.

As stated above, the nature of the unidirectional fibres is not critical, but carbon and aromatic polyamide fibres are preferred. Mixtures of unidirectional fibres may also be used, for example, blends of carbon and glass, or aromatic polyamide and glass.

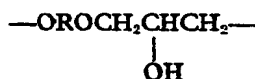
The fibrous material having structural integrity may be woven or non-woven, natural or synthetic, such as nylon in woven or spun bonded form, woven silk or cotton cloth, and woven glass cloth, this last being particularly preferred.

The film comprising the thermosettable resin composition may be provided with a strippable backing sheet, e.g., a polyolefin or polyester film or cellulosic paper, on the face opposite to that brought into contact with the reinforcing strands. Manipulation of the film-reinforcing assembly is often easier if the film has tacky surfaces; these may be produced by coating the film with a substance which retains its tackiness during storage of the film at room temperature but which is cured to a hard, insoluble, infusible resin under conditions which will effect a cure of the thermosettable resin of the film. However, films comprising the thermosettable resin compositions, even those containing a thermoplastics resin which is not heat-curable, often possess without additional treatment an adequate degree of tackiness under the conditions employed for impregnating the unidirectional reinforcing material.

The composite may be made by a batch process, the unidirectional strands and the fibrous web material being laid on the continuous film comprising the thermosetting resin composition which is preferably under slight tension, then a second such continuous film may, if desired, be laid on top, and the assembly is pressed whilst being heated.

The composite may also be made continuously, such as by contacting the unidirectional strands and the fibrous web material with the continuous film of the thermosettable resin composition, and, if desired, applying a second such continuous film to the reverse side of the strands and the fibrous web material, and then applying heat and pressure. More conveniently, two continuous films comprising the thermosettable resin composition, which preferably are supported on the reverse sides by belts or strippable sheets, are applied simultaneously to the unidirectional strands and fibrous web material so as to contact each exposed face. When two continuous films of thermosettable resin are applied, these may be the same or different.

The thermosettable resin composition, which will include a curing agent, may contain a single thermosettable resin, such as an epoxide resin (i.e., a substance containing on average more than one 1,2-epoxide group per molecule) or a resole (formed from a phenol such as phenol itself and an aldehyde such as formaldehyde) or it may contain a mixture of thermosettable resins. Preferably it also contains a thermoplastics resin which is not heat-curable. Examples of such compositions are resoles with, as the thermoplastics component, a poly(vinyl acetal) or a nylon; a novolac (formed from a phenol such as phenol itself and formaldehyde or other aldehyde) with, as the thermoplastics component, a neoprene rubber or an acrylonitrile rubber; and epoxide resins, with, as the thermoplastics component, a phenoxy resin (i.e., a polyarylene polyhydroxy polyether, substantially free from 1,2-epoxide groups, being a copolymer of a dihydric phenol with either a diglycidyl ether of a dihydric phenol or with epichlorohydrin and containing recurring units represented by the formula



where R denotes an arylene group), with a polysulphone (a substance containing recurring units represented by the formula



where R has the meaning previously assigned), or with a copolymer of an  $\alpha$ -olefin

hydrocarbon with an  $\alpha$ -olefin which is an ester of a carboxylic acid. These compositions are made into film adhesives in a conventional manner.

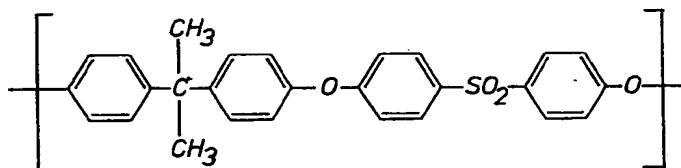
The following Examples illustrate the invention; all parts are by weight.

The materials used were as follows:

"Epoxide resin A" denotes a polyglycidyl ether prepared in a known manner from 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin in the presence of alkali, having an epoxide content in the range 5.0—5.2 equiv./kg. and a viscosity at 21°C in the range 20—40 Pas.

"Epoxide resin B" denotes a polyglycidyl ether prepared in a known manner by reaction of 2,2-bis(4-hydroxyphenyl)propane with epichlorohydrin in the presence of alkali. It had a 1,2-epoxide content in the range 0.25 to 0.42 equiv./kg. and a Durrans softening point of 145°C to 155°C.

"Polysulphone A" denotes a material available from union Carbide Corporation under the designation Polysulphone P1700; according to the manufacturer, it melted in the range 350 to 370°C, its heat deflection temperature (ASTM Specification D648) was 175°C, and it contained, per molecule, 50 to 80 repeating units of the formula



#### EXAMPLE 1

A mixture of Epoxide resin A (100 parts), Polysulphone A (70 parts), and boron trifluoride-monoethylamine complex (5 parts) was dissolved in methylene chloride (120 parts), and the solution was poured onto a 400 mm wide strip of silicone-coated release paper, then warmed gently to evaporate the solvent. The solvent-free film remaining weighed 50 g per square metre.

A layer of unidirectional carbon fibres and an open weave glass scrimcloth were fed, together with two such films of resin, through the nip of a series of heated rollers, the carbon fibres contacting one such film and the scrimcloth contacting the other film, the fibres and scrimcloth also being in contact with each other. The carbon fibres comprised 46 tows spread evenly over a width of 300 mm, each tow comprising 10000 filaments. The scrimcloth, which was also 300 mm wide, weighed 37 g per square metre, was 0.038 mm thick, and had 20.5 warp threads and 19.7 weft threads per 10 mm. The rollers were heated at 110°C and imparted a pressure of 350 kPa. Passage through these rollers took approximately one minute, during which time impregnation of the carbon fibres and scrimcloth took place.

Both sheets of release paper were then removed and the resultant prepreg was easily handled, requiring no special care to maintain its integrity. It could be formed into multilayer laminates and cured by heating at 150°C for 1 hour.

#### EXAMPLE 2

Epoxide resin A (80 parts) and Epoxide resin B (80 parts) were heated at 150°C in a Z-blade mixer. When the mixture was homogeneous it was cooled to 100°C and a milled mixture of Epoxide resin A (20 parts), "Aerosil" (5 parts), and dicyandiamide (12 parts) was incorporated ("Aerosil" is a registered Trade Mark and denotes a finely divided silica of large specific surface area). This mixture was cast onto a sheet of polypropylene 400 mm wide to leave a resin film weighing 50 g/m<sup>2</sup>.

A layer of unidirectional fibres of a poly(p-phenylene terephthalamide) and a layer of open weave glass scrimcloth were fed, together with two such resin films, through the nip of a series of heated rollers, the unidirectional fibres contacting one such film and the scrimcloth the other.

The layer of unidirectional fibres was 300 mm wide and comprised 42 tows, each tow comprising 1000 filaments and weighing 0.79 g/m. The scrimcloth was as described in Example 1. The rollers were heated at 100°C, and imparted a pressure of 500 pKa. Passage through these rollers took approximately one minute, during which time impregnation of the unidirectional fibres and the scrimcloth took place.

Both sheets of polypropylene were then removed and the resultant prepreg

required no special care to maintain its integrity. It could be formed into multilayer laminates and cured by heating at 120°C for 1 hour.

### EXAMPLE 3

Aqueous phenol (80%, 85 g.) and aqueous formaldehyde solution (40%, 85 ml.) where heated at refluxing point in the presence of 0.5 g. of sodium hydroxide until a sample of the reaction mixture separated into two phases if diluted at 20°C with more than its own volume of water. The resin ('Phenolic resin A') was applied to a polyethylene facing sheet at 27 g. per sq. metre and immediately, before the applied film spontaneously broke up into droplets, powdered poly(vinyl formal) was sprinkled onto it at 34 g. per sq. metre. A similar procedure was carried out on a second facing sheet of polyethylene, and the two coated surfaces were then placed in contact and pressed at about 3430 kPa for 1 minute at room temperature. One facing sheet was removed, and the film adhesive was provided with a tacky layer as follows.

The film adhesive was passed under a doctor blade with a clearance of 0.075 mm and coated with a composition which comprised 300 parts of a resin obtained by evaporating Phenolic resin A until the content of resin-forming materials was 90%, 150 parts of polyoxypropylene glycol having an average molecular weight of 1025, 4.5 parts of powdered poly(vinyl butyral), 10.5 parts of "Aerosil", and 100 parts of industrial methylated spirits. The solvent was evaporated from the coating by infra-red lamps, and the film wound on itself, the strippable polyethylene sheet acting as a separator.

To prepare a prepreg of this invention, two such films with a flat bundle of unidirectional E-glass fibres (96 tows, each of 600 tex) sandwiched between are passed continuously through the nip of a series of rollers heated at about 110°C and exerting a pressure of about 350 kPa, the passage taking approximately 30 seconds.

One of the polyethylene sheets is then removed and a glass scrimcloth, as described in Example 1, is contacted with the unidirectional glass fibre. Another polyethylene sheet is placed over the scrimcloth and the structure is passed through a series of heated rollers similar to those used previously, passage again taking 30 seconds, to impregnate the glass fibres and the scrimcloth.

Both sheets of polyethylene are then removed, and the resultant prepreg is easily handled and retains its integrity. It could be formed into multilayer laminates and cured by heating at 170°C for 30 minutes.

### WHAT WE CLAIM IS:—

1. A method of making a reinforced composite which comprises bringing together an essentially solid continuous film comprising a thermosettable resin composition strands of unidirectional reinforcing material, and a layer of fibrous material having structural integrity, under conditions such that the resin composition flows about the strands and fibrous material and forms a coherent curable structure.

2. A method according to claim 1, wherein the resin composition is caused to flow about the strands and fibrous material by applying heat.

3. A method according to claim 1 or 2, in which the resin is caused to flow about the strands and fibrous material by applying pressure.

4. A method according to any of claims 1 to 3, in which the unidirectional reinforcing material is glass, boron, carbon, or polyamide fibres, or metal filaments.

5. A method according to claim 4, in which the unidirectional reinforcing material is aromatic polyamide fibres.

6. A method according to any of claims 1 to 5, in which the layer of fibrous material having structural integrity is nylon in woven or spun-bonded form, woven silk or cotton cloth, or woven glass cloth.

7. A method according to any of claims 1 to 6, in which the film comprising the thermosettable resin composition is provided with a strippable backing sheet on the face opposite to that brought into contact with the reinforcing strands.

8. A method according to any of claims 3 to 7, in which the unidirectional strands and fibrous web material are laid on a continuous film comprising the thermosettable resin composition, then a second such continuous film is laid on top, and the assembly is pressed whilst being heated.

9. A method according to any of claims 3 to 8, in which the composite is made continuously by contacting the unidirectional strands and the fibrous web material with the continuous film of thermosettable resin composition, applying a

second such continuous film to the reverse side of the strands, and applying heat and pressure.

10. A method according to claim 9, in which the two continuous films comprising the thermosettable resin composition are applied simultaneously to the uni-directional strands and fibrous web material.

11. A method according to any of claims 1 to 10, in which the thermosettable resin composition contains an epoxide resin or a resole formed from a phenol and an aldehyde.

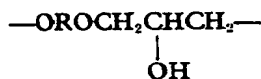
12. A method according to any of claims 1 to 11, in which the thermosettable resin composition contains a thermoplastics resin which is not heat-curable.

13. A method according to claim 12, in which the thermosettable resin composition contains a resole and a poly(vinyl acetal) or a nylon.

14. A method according to claim 12, in which the thermosettable resin composition contains a novolac, formed from a phenol and an aldehyde, with a neoprene rubber or an acrylonitrile rubber.

15. A method according to claim 12, in which the thermosettable resin composition contains an epoxide resin and a thermoplastics component which is

(a) a polyarylene polyhydroxy polyether, substantially free from 1,2-epoxide groups and is a copolymer of a dihydric phenol with either a diglycidyl ether of a dihydric phenol or with epichlorohydrin and contains recurring units represented by the formula



where R denotes an arylene group, or

(b) a polysulphone containing recurring units represented by the formula



where R denotes an arylene group, or

(c) a copolymer of an  $\alpha$ -olefin hydrocarbon with an  $\alpha$ -olefin which is an ester of a carboxylic acid.

16. A method according to any preceding claim, wherein the resin is advanced to the B-stage.

17. A method according to claim 16, in which the resin is subsequently converted into the fully cured, insoluble, and infusible C-stage after the composite has been formed into some desired configuration.

18. A method according to any of claims 2 to 17, in which the resin composition is caused to flow by heating at a temperature of 50° to 180°C.

19. A method according to claim 18, in which the composition is heated at a temperature of 100° to 140°C.

20. A method according to any of claims 3 to 19, in which the resin composition is caused to flow by application of a pressure of 150 to 1000 kPa.

21. A method according to claim 20, in which a pressure of 300 to 600 kPa is applied.

22. A method according to claim 1, substantially as described herein.

23. A method according to claim 1, substantially as described in Example 1.

24. A method according to claim 1, substantially as described in Example 2 or

25. Reinforced composites made by a method as claimed in any of claims 1 to 17 and 23.

26. Reinforced composites made by a method as claimed in any of claims 18 to 22 and 24.

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